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Synthesis of 9,10-dihydrosilaanthracenes with substituents *ortho* to the silicon and methylene bridges

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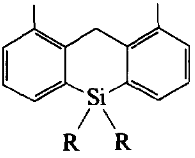
Abstract

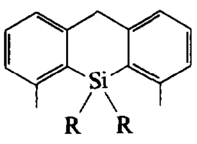
The generation of 9,10-dihydrosilaanthracenes with substituents on benzo ring carbons, specifically in the 4,5-positions adjacent to the methylene bridge, has been developed. Attempts to prepare the 1,8-isomer where the substituents are adjacent to the silicon bridge are also described. The diarylmethane precursors to the substituted 9,10-dihydrosilaanthracenes required the synthesis of 2,3-dihalotoluenes as well as isomeric 2,6-disubstituted benzaldehydes which were then condensed to diarylmethanols through the Grignard reagents. Ring closure to the 4,5-dimethyl-9,9-dialkyl-9,10-dihydro-9-silaanthracene, I, required the use of Rieke magnesium. The structure of I (alkyl = ^{i}Pr) was determined and demonstrates that the introduction of substituents adjacent to the methylene bridge causes the dihydrosilaanthracene framework to become nearly planar with a dihedral (or butterfly) angle of 170 ° C.

Introduction

Dihydrosilaanthracene derivatives with various substituents on the silicon heteroatom or at the methylene bridge have been reported previously [1]. These silaanthracenes exhibit a butterfly conformation and are fluxional in solution [1,2]. There are no current examples of the basic silaanthracene framework with substituents on the benzo ring carbons. More rigid silaanthracenes could conceivably be generated through the introduction of substituents on the benzo groups in positions *ortho* to the silicon and/or methylene positions, that is, adjacent to the ring junctions. Alternatively, substituents in these positions might ultimately stabilize a silaanthracene since it has been shown recently that incorporation of two benzyl groups either in the 10-position or in the 9,10-positions does not provide steric protection for silaanthracene as was observed in the case of the phospha- and arsaanthracene series [3a].

Described in this report are the successful incorporation of substituents *ortho* to the methylene bridge, I, and the attempts to prepare the isomer, II, in which the ring substituents are *ortho* to the silicon heteroatom. In addition, the unsymmetrically substituted silaanthracene, III, has been prepared.


(I)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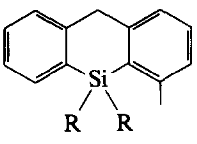

(III)

Experimental

General

All reactions that involved Grignard reagents and chlorosilanes were carried out under an atmosphere of argon or nitrogen in glassware that had been dried at 120 °C for 24 h.

The commercial reagents, 2-chloro-*m*-xylene, 2-nitropropane, *o*-bromochlorobenzene, dichlorodimethylsilane, and dichlorodiisopropylsilane were used as supplied. *N*-Bromosuccinimide was recrystallized from water prior to use. Bis(*o*-chlorophenyl)methane was prepared according to literature methods [4].

Diethylether and tetrahydrofuran (THF) were freshly distilled from sodium/benzophenone under nitrogen. Acetonitrile was dried by distillation from phosphorous pentoxide.

Proton and carbon-13 spectra were recorded in $CDCl_3$ on a Varian XL-300 Spectrophotometer with the residual protons of the deuterated solvent used as the internal standard at 7.24 ppm or relative to TMS when specified. The characteristic solvent peaks centered at 77.0 ppm for carbon were used as the internal reference in the carbon NMR spectra. For low temperature work, the probe was cooled with liquid nitrogen and sample concentrations were 30 mg/ml solvent used in 5 mm (o.d.) XR-55 tubes. Mass spectral data were obtained on a Hewlett-Packard 5988A GC/MS system. Melting point determinations were obtained on a Mel–Temp or Hoover oil bath apparatus and are uncorrected.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

2-Bromo-3-chlorotoluene, IVa. Sodium nitrite solution (50 g $NaNO_2$/88 ml H_2O) was added to a cold (0 °C) mixture of HBr (48%, 210 ml) and 2-chloro-6-methylaniline (100 g, 0.71 mol) and stirred slowly over a 45 minute period while keeping the temperature below 10 °C. Small, continuous additions (30 min) of the diazonium salt were then made to a boiling mixture of 48% HBr (30 ml) and CuBr (26.3 g, 0.183 mol). Steam distillation carried out with additional portions of water provided a tangerine orange oil (85 ml) which was collected from the distillate and separated from the aqueous layer. The oil, washed 4 × with 15 ml portions of concentrated sulfuric acid, once with 100 ml water, 2 × with 50 ml 5% NaOH, and again with 100 ml water, was then dried over magnesium sulfate. Kugelrohr distillation provided the product (110 g, 72%), b.p. 100–105 °C/25 mm. ^1H NMR δ(ppm): 2.47 (s, 3H, CH_3), 7.1–7.3 (m, 3H, Ar). ^{13}C NMR δ(ppm): 24.3, 124.8, 127.5, 127.6, 128.6, 134.8, 140.5. *m/e* (based on ^{79}Br and ^{35}Cl) 204 (M^+).

3-Bromo-2-chlorotoluene, IVb. A mixture of 5-bromo-4-chloro-3-methylbenzenesulfonic acid (14 g, 0.05 mol), prepared by the literature route [5], in 85% phosphoric acid (250 ml) was placed in a round bottom flask equipped with a modified Dean-Stark trap. The solution was refluxed overnight and as water was removed, the temperature of the slurry increased. When the temperature exceeded 200 ° C, a pale yellow liquid began to steam distill. The mixture was left to reflux and the organic layers collected over a period of 5 days. The oil was dissolved in methylene chloride, dried over anhydrous sodium sulfate and the solvent evaporated to give a strong smelling, yellow oil (6.5 g crude, 63%). GC/MS showed the presence of three components: $C_7H_5Cl_2$ ($m/e = 160$, M^+ based on ^{35}Cl), C_7H_5BrCl ($m/e = 204$, M^+ based on ^{79}Br and ^{35}Cl) and $C_7H_5Br_2$ ($m/e = 250$, M^+ based on ^{79}Br) in a 1 : 2 : 1 ratio. The relative ratios varied from run to run. Attempts to separate the dihalides by chromatography or by distillation were unsuccessful. A small fraction with C_7H_5BrCl as a major component was obtained from one of the runs. ^{1}H NMR δ(ppm) in DMSO-d_6: 2.38 (s, 3H, CH_3), 7.16 (t, $J = 7.5$ Hz, 1H), 7.34 (d, $J = 7.5$ Hz, 1H), 7.58 (d, $J = 7.5$ Hz, 1H); ^{13}C NMR δ(ppm) in DMSO-d_6: 21.05, 122.02, 128.12, 130.28, 131.47, 131.57, 138.24.

2-Chloro-3-methylbenzaldehyde, Vb. A solution of 2-chloro-*m*-xylene (47 ml, 0.36 mol) and *N*-bromosuccinimide (63.3 g, 0.36 mol) in carbon tetrachloride (200 ml) was allowed to reflux overnight after using a sun lamp to initiate the reaction. Upon completion, the succinimide was removed by gravity filtration and the filtrate evaporated to give a pale yellow liquid which was distilled under reduced pressure through a 6″ Vigreaux column to provide the product, b.p. 75–79 ° C/0.2 mmHg (44 g, 0.20 mol, 57%). ^{1}H NMR δ(ppm): 2.45 (s, 3H, CH_3); 4.60 (s, 2H, CH_2); 7.32 (m, 3H, Ar).

Sodium metal (4.9 g, 0.21 mol) was dissolved in absolute ethanol (250 ml) under an atmosphere of argon. To this solution, 2-nitropropane (24 g, 0.27 mol) and 2-chloro-3-methylbenzylbromide (22 g, 0.10 mol) were added. The mixture was left to stir overnight, filtered and the solvent evaporated. The product was washed with a 1 : 1 mixture of diethyl ether and water, 10% sodium hydroxide, and water and dried over anhydrous sodium sulfate. Vacuum distillation gave a pale yellow liquid, b.p. 60–65 ° C/6.0 mmHg (31 g, 77%). ^{1}H NMR δ(ppm): 2.40 (s, 3H, CH_3); 7.45 (m, 3H, Ar); 10.5 (s, 1H, CHO); ^{13}C NMR δ(ppm): 19.8, 126.7, 127.0, 132.7, 136.4, 137.7, 190.5. m/e 154 (M^+, based on ^{35}Cl). The aldehyde was characterized further through conversion to the benzoic acid derivative, m.p. 140–141 ° C. Anal. Found: C, 56.13; H, 4.21. $C_8H_7O_2Cl$ calcd.: C, 56.32; H, 4.14%.

2-Chloro-6-methylbenzaldehyde, Va. A sodium nitrite solution (41 g $NaNO_2$ in 59 ml H_2O) was added to a cold (0 ° C) mixture of concentrated HCl (135 ml) and 2-chloro-6-methylaniline (83 g, 0.59 mol) with stirring over a period of 60 min, while the temperature was held below 10 ° C. The diazonium salt was then neutralized to a pH of 6–7 with a sodium acetate solution (52 g $NaC_2H_3O_2$ in 82 ml H_2O).

A formaldoxime reagent was prepared immediately before use by heating hydroxylamine hydrochloride (62 g, 0.89 mol, in 400 ml water) with paraformaldehyde (27 g) until a clear solution resulted. Additional sodium acetate (120 g) was added before the mixture was heated to boiling under reflux (15 min). To the cooled formaldoxime reagent (10–15 ° C), hydrated copper(II) sulfate (15 g, 0.090 mol), anhydrous sodium sulfite (2.4 g, 0.20 mol) and sodium acetate (390 g in 425 ml H_2O) was added.

The diazonium salt was introduced to the formaldoxime reagent below the surface of the solution with stirring, keeping the temperature between 10–15 ° C. The solution, after being stirred at the same temperature for 2 h, was made neutral with concentrated HCl and an additional 540 ml of concentrated HCl added. The resultant solution was boiled under reflux for 4 h. Steam distillation provided an orange organic layer. After neutralization of the distillate with $NaHCO_3$ and extraction with ether (1600 ml), the volatiles were removed. Sodium bisulfite solution (210 ml, 40%) was added to the oil with shaking and the mixture allowed to stand overnight. The aqueous solution, to which additional water (650 ml) had been added, was extracted with ether (210 ml) to remove impurities. The aldehyde, regenerated from the aqueous layer by boiling with a solution of concentrated sulfuric acid and water (1 : 1, 212 ml) for 30 min, was isolated after extraction with 700 ml ether and yielded 42 g of orange liquid. Impure solid formed upon standing and was purified by vacuum distillation, b.p. 101–103° C/26 mm Hg, followed by recrystallization to give pure crystals, m.p. = 35 ° C (31 g, 35%). ^{1}H NMR δ(ppm): 2.40 (s, 3H, CH_3), 7.00–7.40 (m, 3H, Ar), 10.55 (s, 1H, CHO). ^{13}C NMR δ(ppm): 21.2, 128.2, 130.6, 133.5, 139.0, 142.4, 192.3. m/e (based on ^{35}Cl) 154 (M^+). The 2,4-dinitrophenylhydrazone derivative was prepared for analysis. Found: C, 50.36; H, 3.27. $C_{14}H_{12}N_4O_4Cl$ calcd.: C, 50.01; H, 3.60%.

Bis(2-chloro-6-methylphenyl)methanol, VIa. n-Butyllithium (45 ml, 1.6 M in hexanes) was added dropwise to 2-bromo-3-chloro-toluene (14 g, 0.070 mol) in 1 : 1 THF/ether (70 ml) over a period of 30 min with stirring, while the temperature was kept below − 95 ° C with a toluene slush bath. After stirring for 30 min a solution of 2-chloro-6-methylbenzaldehyde (11 g, 0.70 mol) in ether (90 ml) was added maintaining the temperature below − 95 ° C. The solution was then allowed to warm to room temperature overnight. After hydrolytic workup with saturated ammonium chloride and extraction with ether, the organic layer was dried over magnesium sulfate. Removal of volatiles yielded a solid product after Kugelrohr distillation, b.p. 140–145 ° C/0.15 mmHg (16 g, 82%). Recrystallization from hot 95% ethanol yielded crystals, m.p. 148 ° C. ^{1}H-NMR δ(ppm): 2.37 (bs, 6H, CH_3), 2.71 (s, 1H, OH), 6.73 (s, 1H, C*H*OH), 7.05–7.30 (m, 6H, Ar). ^{13}C NMR δ(ppm): 21.2, 73.3, 128.18, 128.24, 130.7, 133.8, 137.5, 139.6. m/e (based on ^{35}Cl) 280 (M^+). Anal. Found: C, 64,33; H, 4.95. $C_{15}H_{14}Cl_2O$ calcd.: C, 64.07; H, 5.02%.

(2-Chloro-3-methylphenyl)(2-chlorophenyl)methanol, VII. Magnesium mesh (1.9 g, 0.079 mol) was placed in a round bottom flask and covered with dry ether under an atmosphere of argon. A solution of *o*-bromochlorobenzene (14 g, 0.073 mol) and two drops of ethylene dibromide in diethyl ether (50 ml) was added dropwise using a cold water bath to moderate the reflux rate. Upon completion, an additional 50 ml of diethyl ether were added. This solution was left to reflux overnight and the Grignard solution was then cannulated into an addition funnel of a second round bottom flask containing 2-chloro-3-methylbenzaldehyde (14 g, 0.093 mol) in 40 ml ether. The Grignard was added dropwise to the aldehyde and the resulting solution was left to stir overnight before hydrolysis with saturated aqueous ammonium chloride. The ether layer was dried over anhydrous sodium sulfate and after removal of the volatiles, Kugelrohr distillation provided the product, b.p. 130–140 ° C/0.1 mmHg (7.4 g, 38%). Recrystallization from absolute ethanol provided white needles, m.p. 95–96 ° C. ^{1}H NMR δ(ppm): 2.40 (s, 3H, CH_3), 2.50 (d, 1H, OH), 6.56 (d, 1H, C*H*OH), 7.15–7.41 (m, 7H, Ar). ^{13}C NMR δ(ppm): 20.6, 70.0, 125.7, 126.4, 128.3,

129.0, 129.5, 130.4, 133.35, 133.41, 136.7, 139.48, 139.52. m/e 266 (M^+, based on ^{35}Cl); 153, 139. Anal. Found: C, 62.92; H, 4.67. $C_{14}H_{12}Cl_2O$ calcd.: C, 62.92; H, 4.49%.

Bis(2-chloro-6-methylphenyl)methane, VIII. Dichlorodimethylsilane (12 g, 0.090 ml) was added dropwise via syringe to a slurry of bis(2-chloro-6-methylphenyl)-methanol (12 g, 0.043 mol) and sodium iodide (26.9 g) in acetonitrile (45 ml), with stirring under nitrogen. An immediate dark brown color change occurred and the mixture was allowed to stir under nitrogen overnight (20.5 h). The reaction mixture was diluted with ethyl acetate (450 ml) then washed 2 × with 100 ml portions of water, 2 × with 100 ml saturated sodium bicarbonate solution, 4 × with 100 ml 10% sodium thiosulfate solution and finally 2 × with a brine solution. Liquid siloxanes were physically separated from the solid product using a glass pipet. Purification was accomplished by recrystallization from hot 95% ethanol which yielded the diarylmethane, m.p. 119 °C (7.8 g, 69%). ^{1}H NMR δ(ppm): 2.06 (s, 6H, CH_3), 4.49 (s, 2H, CH_2), 7.00–7.60 (m, 6H, Ar). ^{13}C NMR δ(ppm): 20.6, 32.5, 127.1, 127.4, 129.4, 135.2, 136.0, 139.5. m/e 264 (M^+, based on ^{35}Cl). Anal. Found: C, 67.43; H, 5.19. $C_{15}H_{14}Cl_2$ calcd.: C, 67.94; H, 5.32%.

(2-Chloro-3-methylphenyl)(2-chlorophenyl)methane, IX. Sodium iodide (9.6 g, 64 mmol) was slurried with (2-chloro-3-methylphenyl)(2-chlorophenyl)methanol (4.6 g, 17 mmol) in 30 ml dry acetonitrile under an atmosphere of argon. Dichlorodimethylsilane (4.1 g, 32 mmol) was added dropwise and the reaction mixture was left to stir overnight. The mixture was then diluted with ethyl acetate (160 ml) and the solution was washed with water, saturated aqueous sodium bicarbonate, 10% aqueous sodium thiosulfate and brine. The solvent was evaporated and Kugelrohr distillation of the residue provided a colorless liquid, b.p. 104–105 °C/0.1 mmHg (3.7 g, 87%). ^{1}H NMR δ(ppm): 2.42 (s, 3H, CH_3); 4.22 (s, 2H, CH_2); 6.84–7.42 (m, 7H, Ar). ^{13}C NMR δ(ppm): 20.8, 37.3, 126.2, 126.8, 127.7, 128.1, 129.1, 129.4, 130.6, 134.4, 134.6, 137.2, 137.3.

4,5,9,9-Tetramethyl-9,10-dihydro-9-silaanthracene, Ia. Activated magnesium was prepared by mixing $MgCl_2$ powder (1.7 g, 18 mmol), potassium metal (1.3 g, 32 mmol), and potassium iodide (2.5 g, 15 mmol) in THF (20 ml) followed by reflux for 2 h. To the warm reaction mixture was added bis(2-chloro-6-methylphenyl)methane (2.0 g, 7.6 mmol) in THF (15 ml) dropwise with stirring. The resulting mixture was allowed to reflux an additional 90 min. Dichlorodimethylsilane (1.0 g, 7.8 mmol) was added directly to the warm reaction mixture slowly via syringe over 15 min with stirring. After 7.5 h at reflux, GC analysis of a hydrolyzed aliquot showed a 60% formation of the silaanthracene. The reaction mixture, quenched with saturated ammonium chloride solution, washed three times with water, and stripped of volatiles to produce a yellow-brown mass containing siloxanes. The product was obtained after flash chromatography over silica gel (100–200 mesh) with 5% ether/hexanes followed by recrystallization from absolute ethanol to yield solid Ia (0.20 g, 12%) m.p. 78 °C. ^{1}H NMR δ(ppm): 0.45 (s, 6H, $SiCH_3$), 2.48 (s, 6H, CH_3), 4.06 (s, 2H, CH_2), 7.15–7.50 (m, 6H, Ar). ^{13}C NMR δ: −2.32, 20.65, 32.19, 125.5, 131.0, 131.1, 134.9, 135.5, 144.0. m/e 252 (M^+). Anal. Found: C, 80.46; H, 7.89. $C_{17}H_{20}Si$ calcd.: C, 80.89; H, 7.99%.

9,9-Diisopropyl-4,5-dimethyl-9,10-dihydro-9-silaanthracene, Ib. Ib was prepared in a similar fashion from $MgCl_2$ powder (1.73 g, 18.1 mmol), potassium metal (1.24 g, 31.7 mmol), potassium iodide (2.5 g), bis(2-chloro-6-methylphenyl)methane (2.0 g, 7.6 mmol) and dichlorodiisopropylsilane (1.5 g, 8.0 mmol). ^1H NMR δ(ppm): 1.00 (d, 6H, CH_3), 1.45 (sep, 1H, CH), 2.45 (s, 3H, CH_3), 4.00 (s, 1H, CH), 7.15–7.50 (m, 3H, Ar). ^{13}C NMR δ(ppm): 12.8, 18.2, 20.9, 34.1, 125.3, 131.0, 131.4, 132.0, 136.1, 144.5. *m/e* 308 (M^+). Anal. Found: C, 81.83; H, 9.04. $C_{21}H_{28}Si$ calcd.: C, 81.75; H, 9.15%.

1,9,9-Trimethyl-9,10-dihydro-9-silaanthracene, IIIa. Magnesium mesh (1.5 g, 60 mmol) was added to a round bottom flask, covered with dry tetrahydrofuran and the mixture heated to reflux. A mixture of (2-chloro-3-methylphenyl)(2-chlorophenyl)methane (4.0 g, 20 mmol), a drop of ethylene dibromide and dry THF (35 ml) was added dropwise. The mixture was left to reflux for 22 h and dichlorodimethylsilane (2.1 g, 20 mmol) in dry THF (15 ml) was added dropwise. The solution was refluxed for 3 h, left to stir overnight then hydrolyzed with saturated aqueous ammonium chloride. The organic layer was dried over anhydrous sodium sulfate and the solvent evaporated. Kugelrohr distillation provided a viscous liquid, b.p. 100–120 °C/0.05 mmHg (1.3 g, 33%) which solidified. Recrystallization from absolute ethanol provided fine, white crystals, m.p. 62–63 °C. ^1H NMR δ(ppm): 0.55(s, 6H, $SiMe_2$); 2.54 (s, 3H, CH_3); 4.14 (s, 2H, CH_2); 7.08–7.34 (m, 6H, Ar); 7.62 (d, 1H, Ar). ^{13}C NMR δ(ppm): −1.16, 23.9, 42.1, 125.7, 126.0, 127.4, 127.6, 129.1, 133.2, 133.9, 135.6, 143.8, 145.6, 146.2. *m/e* 238 (M^+), 223. Anal. Found: C, 80.88; H, 7.92. $C_{16}H_{18}Si$ calcd.: C, 80.67; H, 7.56%.

9,9-Diisopropyl-1-methyl-9,10-dihydro-9-silaanthracene, IIIb. In a similar fashion IIIb was prepared from magnesium mesh (1.6 g, 70 mmol), (2-chloro-3-methylphenyl)(2-chlorophenyl)methane (4.2 g, 20 mmol) and dichlorodiisopropylsilane (3.1 g, 20 mmol). After a 52 h reflux period the mixture was hydrolyzed with saturated aqueous ammonium chloride and the organic layer was dried over anhydrous sodium sulfate. Removal of the volatiles and Kugelrohr distillation provided an oil, b.p. 105–125 °C/0.1 mmHg (0.41 g, 7%) which solidified. Recrystallization from absolute ethanol provided coarse, white crystals, m.p. 41–42 °C. ^1H NMR δ(ppm): 0.94 (d, 6H, CH_3); 1.13 (d, 6H, CH_3); 1.62 (sep, 2H, CH); 2.53 (s, 3H, CH_3); 4.16 (s, 2H, CH_2); 7.05–7.32 (m, 6H, Ar); 7.71 (d, 1H, Ar). ^{13}C NMR δ(ppm): 13.5, 18.6, 18.7, 24.7, 42.7, 124.8, 126.1, 127.6, 127.8, 128.8, 128.9, 131.6, 131.7, 134.7, 143.7, 146.3, 148.8. *m/e* 294 (M^+), 251. Anal. Found: C, 81.21; H, 9.20. $C_{20}H_{26}Si$ calcd.: C, 81.63; H, 8.84.

9,9-Diisopropyl-9,10-dihydro-9-silaanthracene, X. Magnesium mesh (1.9 g, 80 mmol) was placed in a round bottom flask, covered with THF and heated to reflux. A mixture of bis-*o*-chlorophenylmethane (5.0 g, 20 mmol), one drop of ethylene dibromide and THF (20 ml) was added dropwise. The reaction mixture was refluxed for 3 h, stirred at room temperature overnight and then refluxed an additional 4.5 h. A solution of dichlorodiisopropylsilane (3.7 g, 20 mmol) in THF (20 ml) was added dropwise. The reaction mixture was refluxed for a total of 18 h and then hydrolyzed with saturated aqueous ammonium chloride. The organic layer was dried over anhydrous sodium sulfate and the solvent evaporated. Kugelrohr distillation provided a white a viscous oil, b.p. 110–135 °C/0.1 mmHg (1.8 g, 32%) which solidified. Recrystallization from absolute ethanol provided large colorless crystals, m.p. 46–47 °C. ^1H NMR δ(ppm): 1.05 (d, 12H, CH_3); 1.47 (sep, 2H, CH); 4.14 (s, 2H, CH_2); 7.20–7.33 (m, 6H, Ar); 7.64 (d, 2H, Ar). ^{13}C NMR δ(ppm): 12.3, 18.1, 41.9, 125.2, 128.3, 129.0, 131.8, 134.1, 146.5. *m/e* 280 (M^+), 237. Anal. Found: C, 81.54; H, 8.93. $C_{19}H_{24}Si$ calcd.: C, 81.43; H, 8.57%.

Table 1

Crystallographic data collection and structure refinement parameters for Ib [a]

Molecular formula	$C_{21}H_{28}Si$
Formula weight, g/mol	308.5
Radiation	Mo-K_α(λ = 0.71069 Å)
Temperature, K	298
Crystal size, mm	0.4×0.2×0.2
Crystal system	Orthorhombic
Space group	*Pbca*
Cell constants	
a, Å	10.665(2)
b, Å	15.284(3)
c, Å	23.433(5)
V, Å^3	3819.7(13)
Z	8
D_{calc}, Mg m^{-3}	1.073
μ, mm^{-1}	0.114
2θ range	4.0 to 45°
Reflections collected	2851
Independent reflections	2493 (R_{int} = 0.00%)
Observed reflections	1165 ($F > 6.0\sigma(F)$)
Ratio data/parameter	5.9 : 1
Absorption correction	N/A
R	5.67%
R_w	5.76%

[a] Estimated standard deviation of least significant digit(s) are given in parentheses for this and subsequent Tables.

Table 2

Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients (Å^2 ×10^3)

	x	y	z	U_{eq} [a]
Si	1268(2)	556(1)	3362(1)	59(1)
C(1)	181(5)	1203(3)	3813(3)	56(3)
C(2)	−826(6)	1652(4)	3569(3)	70(3)
C(3)	−1622(6)	2158(4)	3882(3)	79(3)
C(4)	−1430(7)	2231(4)	4457(3)	77(3)
C(5)	−455(7)	1799(4)	4727(3)	62(3)
C(6)	354(6)	1276(3)	4410(3)	54(2)
C(7)	1406(6)	823(4)	4728(2)	72(2)
C(8)	2215(5)	128(3)	4466(3)	53(3)
C(9)	3000(6)	−312(4)	4837(3)	61(3)
C(10)	3782(6)	−966(5)	4631(3)	78(3)
C(11)	3785(6)	−1186(4)	4061(4)	81(3)
C(12)	3011(6)	−745(4)	3691(3)	70(3)
C(13)	2206(5)	−81(3)	3881(3)	52(2)
C(14)	346(6)	−128(4)	2851(3)	80(3)
C(15)	2348(6)	1311(4)	2964(3)	78(3)
C(16)	1057(6)	−547(4)	2371(3)	121(3)
C(17)	−443(6)	−807(5)	3158(3)	110(4)
C(18)	3236(6)	1789(4)	3356(3)	114(4)
C(19)	1678(6)	1964(4)	2584(3)	119(4)
C(20)	−310(6)	1909(4)	5365(3)	86(3)
C(21)	3076(6)	−114(4)	5469(2)	86(3)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

X-ray diffraction study of Ib. Colorless crystals of compound Ib were grown from absolute ethanol. The crystals were mounted on a glass fibre in random orientation. Preliminary examination and data collection were carried out with Mo-K_α radiation on a Siemens R3 diffractometer. Final cell constants were obtained by least squares analysis of 25 automatically centered reflections ($20 < 2\theta < 25°$). Data were collected by ω scan technique, and the intensity of 3 reflections were monitored every 50 reflections. There was no significant change in intensities of the three standard reflections during data collection. Crystal data and intensity collection parameters are summarized in Table 1.

Data reduction, structure solution and refinement was carried out by SHELXTL-PLUS structure solution software package [7]. The structure was solved by direct methods. Full matrix least squares refinement was carried out by minimizing $\Sigma w(F_o - F_c)^2$. Final positional parameters are given in Table 2. Hydrogen atoms were included at their calculated positions. The final difference Fourier map had a maximum electron density of 0.28 e Å^{-3}. All calculations were performed on a VAX Station II GPX computer.

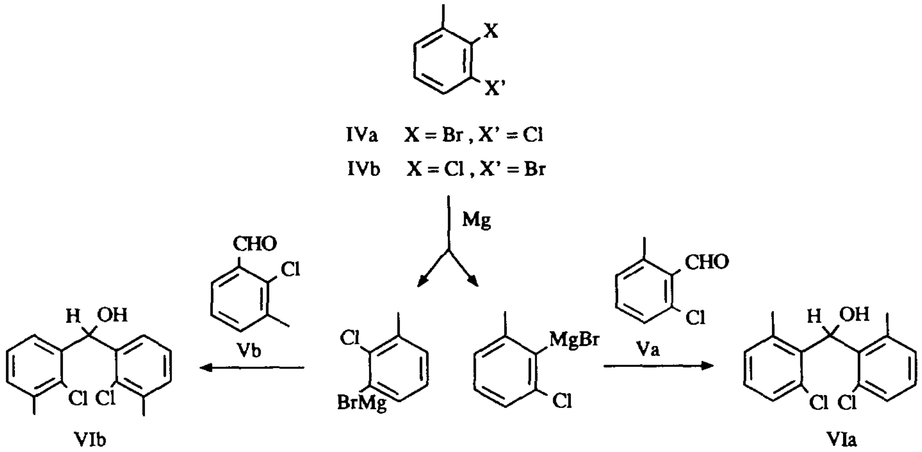
Lists of positional and isotropic temperature factors for H-atoms and calculated and observed structure factors are available from the authors on request.

Results and discussion

The general route to 9,10-dihydrosilaanthracenes involves reaction of the Grignard reagent formed from bis(*o*-chlorophenyl)methane with a dihalosilane [4,6]. The synthetic route to the diarylmethane derivatives that would be the precursors to I and II requires the condensation of 2,3-substituted toluene, IV, with the appropriate benzaldehyde, V, to give the carbinol VI which is then reduced. Of the four tri-substituted compounds IVa, IVb, Va and Vb only IVb had been previously described in the literature [5]. Since no routes which involve directing effects of substituents in disubstituted benzenes are likely to lead directly to the desired 1,2,3-trisubstituted precursors commercial anilines and 2-chloro-*m*-xylene were used as starting points for the required IV and V.

The diazotization of 2-chloro-6-methylaniline followed by coupling with copper(I) bromide provided IVa in good yields. The four step literature route to IVb starts with the sulfonation of *o*-toluidine followed by bromination, introduction of chlorine through diazotization of the amine and finally desulfonation by heating in polyphosphoric acid. Much to our surprise the last step leads to a mixture of IVb as well as to the two products that result from disproportionation, IVc (X = X′ = Cl) and IVd (X = X′ = Br) in a ratio of about 2 : 1 : 1 (IVb : IVc : IVd) although the amounts tended to vary from run to run. Attempts to separate IVb from this mixture were not successful.

The aldehyde was also obtained from 2-chloro-6-methylaniline by reaction of the diazonium salt with formaldoxime, a somewhat obscure method used by Beech and coworkers to produce *ortho*-substituted benzaldehydes [8]. Although the yields are only in the 30–35% range the one step reaction is more efficient than an alternative through carbonation of a Grignard reagent from IVa followed by conversion of the benzoic acid to Va. The aldehyde, Vb was formed from 2-chloro-*m*-xylene in two steps by a route used to prepare an analogous aldehyde [9]. Bromination of the



Scheme 1.

xylene gave 2-chloro-3-methylbenzyl bromide which was converted to the aldehyde through reaction with the sodium salt of 2-nitropropane.

The coupling of IV and V to the carbinol proved to be somewhat difficult. The formation of a Grignard reagent from IVa from a variety of magnesium sources (shavings, mesh, powder) gave a maximum yield of the organometallic between 40–45% as determined from hydrolysis of an aliquot of the reaction mixture. Coupling of IVa and Va was eventually accomplished by reaction of the aryl lithium reagent formed from addition of 2-bromo-3-chlorotoluene to n-butyllithium at low temperature with Va. Formation of a Grignard reagent from the mixture of IVb, IVc and IVd also proved to be difficult. Although lithium reagents could be generated from the mixture too many products were obtained to make separation of reasonable quantities feasible. However, the unsymmetrical methanol, (2-chloro-3-methylphenyl)(2-chlorophenyl)methanol, VII, was produced from the reaction of *o*-chlorophenylmagnesium bromide with Vb.

Previous methods utilized for the reduction of the carbinols that are the precursors to 9,10-dihydrosilaanthracenes involved gaseous hydrogen iodide [6] and hydriodic acid in acetic acid–acetic anhydride [10]. An alternative, recently introduced for diarylmethanols involves the use of the combined reagent, potassium iodide and dichlorodimethylsilane although the method was used on less than a 20 millimole scale [11]. This later method was used to reduce VIa and VII in high yields. Although an excess of dichlorodimethylsilane is required and large quantities of siloxanes are produced the siloxanes can be removed physically or the diarylmethane can be separated from the siloxanes by distillation.

The reaction of various commercial grades of magnesium in THF with bis(2-chloro-6-methylphenyl)methane, VIII, was very slow and showed small conversion to the Grignard reagent even after 72 h at reflux. With activated magnesium prepared by the Rieke method [12] the diGrignard was formed in 65–75% yields after only 2 h as determined by GC analysis of a hydrolyzed aliquot. The silaanthracenes were formed in more than 60% yield but removal of the byproducts was extremely difficult resulting in isolation of less than 15% of I. Ring closure utilizing (2-chloro-3-methylphenyl)(2-chlorophenyl)methane, IX, could be success-

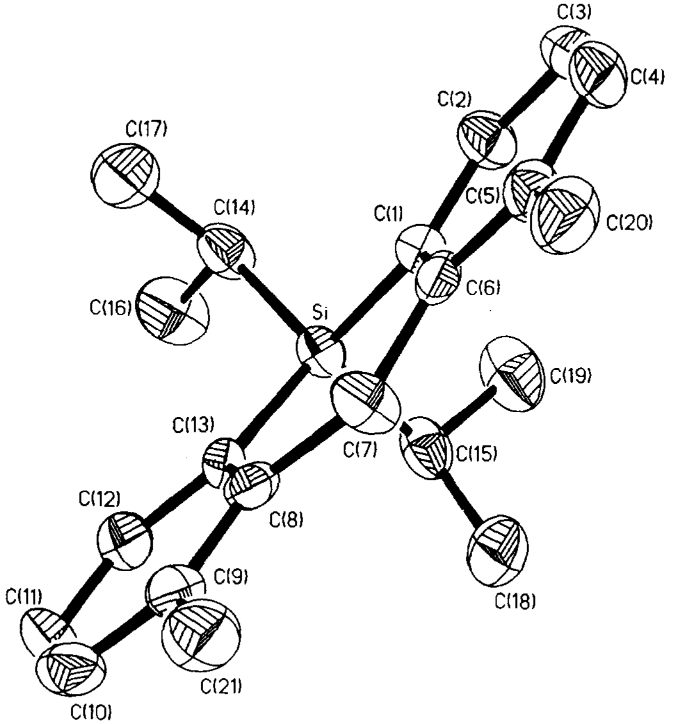
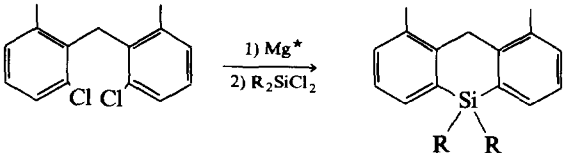


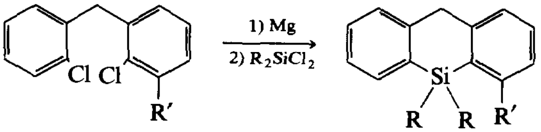
Fig. 1. Projection view of Ib with atom labels.

fully achieved through the use of magnesium mesh. Even one methyl group *ortho* to chlorine introduces sufficient steric bulk that ring closure of IX with dichlorodiisopropylsilane produces less than 10% of the 9,10-dihydrosilaanthracene as compared to 32% in the absence of the methyl group. The ring closure reactions are summarized in Eqs. 1 and 2 for VIII and IX respectively.



(1)

(Ia R = Me; Ib R = ^{i}Pr)



(2)

	R	R′	%
IIIa	Me	Me	33
IIIb	^{i}Pr	Me	7
X	^{i}Pr	H	32

Table 3

Bond lengths (Å) and angles (°) for Ib

Si-C(1)	1.854(6)	Si-C(13)	1.851(6)
Si-C(14)	1.868(7)	Si-C(15)	1.878(6)
C(1)-C(2)	1.398(9)	C(1)-C(6)	1.416(9)
C(2)-C(3)	1.363(9)	C(3)-C(4)	1.367(12)
C(4)-C(5)	1.385(10)	C(5)-C(6)	1.391(9)
C(5)-C(20)	1.512(9)	C(6)-C(7)	1.514(8)
C(7)-C(8)	1.499(8)	C(8)-C(9)	1.381(9)
C(8)-C(13)	1.410(9)	C(9)-C(10)	1.389(10)
C(9)-C(21)	1.515(9)	C(10)-C(11)	1.377(12)
C(11)-C(12)	1.373(10)	C(12)-C(13)	1.400(9)
C(14)-C(16)	1.501(9)	C(14)-C(17)	1.516(9)
C(15)-C(18)	1.509(9)	C(15)-C(19)	1.516(9)
C(1)-Si-C(13)	104.1(3)	C(1)-Si-C(14)	109.5(3)
C(13)-Si-C(14)	114.2(3)	C(1)-Si-C(15)	109.8(3)
C(13)-Si-C(15)	108.5(3)	C(14)-Si-C(15)	110.4(3)
Si-C(1)-C(2)	120.5(5)	Si-C(1)-C(6)	121.6(4)
C(2)-C(1)-C(6)	117.8(5)	C(1)-C(2)-C(3)	122.4(6)
C(2)-C(3)-C(4)	119.0(6)	C(3)-C(4)-C(5)	121.6(6)
C(4)-C(5)-C(6)	119.7(6)	C(4)-C(5)-C(20)	118.4(6)
C(6)-C(5)-C(20)	121.9(6)	C(1)-C(6)-C(5)	119.5(5)
C(1)-C(6)-C(7)	123.0(5)	C(5)-C(6)-C(7)	117.4(6)
C(6)-C(7)-C(8)	123.4(5)	C(7)-C(8)-C(9)	115.9(6)
C(7)-C(8)-C(13)	123.7(5)	C(9)-C(8)-C(13)	120.4(5)
C(8)-C(9)-C(10)	119.7(6)	C(8)-C(9)-C(21)	123.4(6)
C(10)-C(9)-C(21)	116.9(6)	C(9)-C(10)-C(11)	121.0(7)
C(10)-C(11)-C(12)	119.3(6)	C(11)-C(12)-C(13)	121.6(6)
Si-C(13)-C(8)	121.6(4)	Si-C(13)-C(12)	120.3(5)
C(8)-C(13)-C(12)	117.9(5)	Si-C(14)-C(16)	116.9(5)
Si-C(14)-C(17)	111.8(4)	C(16)-C(14)-C(17)	110.0(5)
Si-C(15)-C(18)	112.3(4)	Si-C(15)-C(19)	114.0(5)
C(18)-C(15)-C(19)	109.6(5)		

Room and low temperature (−90 °C) ^{1}H NMR experiments of Ia, Ib and IIIb showed the methylene bridge protons to be singlets at both temperatures. Thus methyl substituents *ortho* to the methylene bridge or one methyl substituent *ortho* to the silicon heteroatom combined with relatively bulky substituents at silicon are not sufficient to increase the barrier to ring inversion of the silaanthracene framework even at −90 °C. Alternatively, the dihydrosilaanthracene framework becomes flattened due to the incorporation of the groups adjacent to the methylene bridge. The crystal structure of Ib was determined in order to determine whether the latter had occurred.

Bond lengths and angles for Ib are provided in Table 3 with the numbering scheme shown in Fig. 1. The tricyclic skeleton exhibits a bend or butterfly angle of 170.3°. The bend angles for the known dihydrosilaanthracene compounds are given in Table 4 and the data clearly demonstrate that the framework in Ib is nearly planar compared to the other dihydrosilaanthracenes which exhibit bend angles near 130° [16*].

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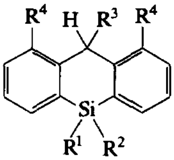
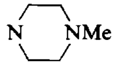
* A reference number with an asterisk indicates a note in the list of references.

Table 4

Dihedral angles in 9,10-dihydro-9-silaanthracenes



R_1	R_2	R_3	R_4	Dihedral angle	Ref.
H	H	H	H	136	13
Me	$(CH_2)_3NMe_2\cdot HCl$	H	H	132	14
Me	Me		H	128	15
^{i}Pr	^{i}Pr	H	Me	170	this work

The presence of two substituents such as in II are probably required to move the barrier into a range where it can be measured. Such an approach has been successful in locking the 10,11-dihydrodibenzo[*b*,*f*]silepin system which contains a central seven-membered ring. The low yields encountered during the formation of IIIb suggest that forming reasonable quantities of II will be a challenging task even when the precursor can be obtained. Incorporation of groups bulkier than methyl in the 4,5- or 1,8-positions introduces an additional difficulty since more complex routes to the 1,2,3-trisubstituted benzene derivatives required to produce the precursors to the heterocycle must be developed.

Acknowledgments

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References

1 J.Y. Corey, Adv. Organomet. Chem., 15 (1975) 139.

2 O.A. D'yachenko and L.O. Atovmyan, Zh. Obsch. Khim., 24 (1983) 144.

3 (a) Y. van den Winkel, O.S. Akkerman, F. Bickelhaupt, Main Group Met. Chem., 11 (1988) 91; (b) Y. van den Winkel, B.L.M. van Baar, H.M.M. Bastiaans, F. Bickelhaupt, M. Schenkel and H.B. Stegmann, Tetrahedron, 46 (1990) 1009.

4 P. Jutzi, Z. Naturforsch. B, 24 (1969) 354.

5 (a) W.P. Wynne, J. Chem. Soc., Trans., 61 (1982) 1040; (b) R.H.C. Nevile, A. Winther, ibid., 37 (1880) 626.

6 P. Jutzi, Chem. Ber., 104 (1971) 1455.

7 G.M. Sheldrick, Siemens Analytical X-Ray Division, Madison, WI, 1989.

8 W.F. Beech, J. Chem. Soc., (1954) 1297.

9 H.B. Hass, M.L. Bender, J. Am. Chem. Soc., 71 (1949) 1767.

10 L.S. Chang and J.Y. Corey, Organometallics, 8 (1989) 1989.

11 J.M. Wiggens, Synth. Commun., 18 (1988) 746.

12 R.D. Rieke, Top. Curr. Chem., 59 (1979) 1.

13 O.A. D'yachenko, L.O. Atovmyan, S.V. Soboleva, Zh. Strukt. Khim., 15 (1976) 191.

14 E.R. Corey, J.Y. Corey, W.F. Paton, and M.D. Glick, Acta Crystallogr., Sect. B, 32 (1976) 2025.

15 J.Y. Corey, M.J. Dye, R.L. Farrell and M.V. Mitchell, J. Organomet. Chem., 153 (1978) 127.

16 *Note added in proof*. The crystal structure of X has been determined and the bend angle is 157.9°. Unpublished work, N. Rath and J.Y. Corey.